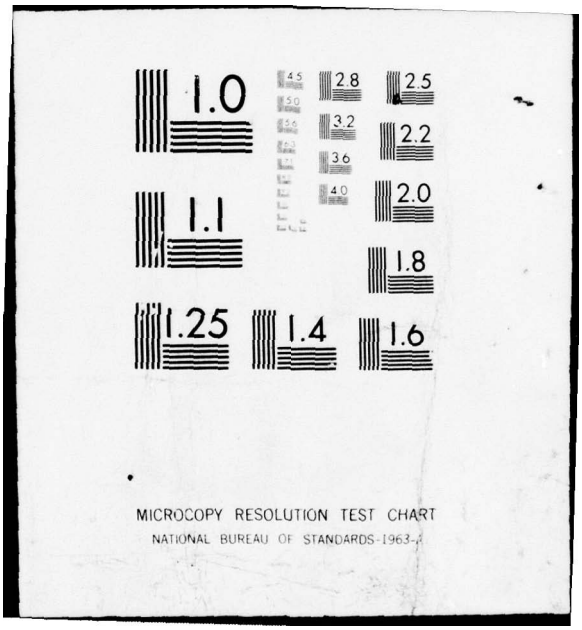
AD-A042 912 HORIZONS RESEARCH INC CLEVELAND OHIO F/G 7/2
POLY(FLUOROORGANOPHOSPHAZENES).(U)
JUL 77 A H GERBER F44620-76-C-0101
UNCLASSIFIED AFOSR-TR-77-0851 NL

OF
AD
A042912

END
DATE
FILMED
9-77
DDC


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AFOSR-TR- 77-0851

(12)
B.S.

POLY(FLUOROORGANOPHOSPHAZENES)

FINAL TECHNICAL REPORT

May 1, 1976 to April 30, 1977

Horizons Research Incorporated
23800 Mercantile Road
Cleveland, Ohio 44122

Arthur H. Gerber

Directorate of Chemical Sciences
Air Force Office of Scientific Research
Building 410
Bolling Air Force Base, DC 20332

Contract No. F44620-76-C-0101

July 1977

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
NOTICE OF TRANSMITTAL TO DDC
This technical report has been reviewed and is approved for public release IAW AFR 190-12 (7b).
Distribution is unlimited.
A. D. BLOSE
Technical Information Officer

POLY(FLUOROORGANOPHOSPHAZENES)

FINAL TECHNICAL REPORT

May 1, 1976 to April 30, 1977

Horizons Research Incorporated
23800 Mercantile Road
Cleveland, Ohio 44122

Arthur H. Gerber

Directorate of Chemical Sciences
Air Force Office of Scientific Research
Building 410
Bolling Air Force Base, DC 20332

Contract No. F44620-76-C-0101

July 1977

POLY(FLUOROORGANOPHOSPHAZENES)

ABSTRACT

Novel cyclic and polymeric acetylenicphosphazenes of approximate structure $[(C_6H_5C\equiv C)_2PN]_x$ have been prepared by the reaction of alkali phenylacetylide salts and dichlorophosphazenes, $[Cl_2PN]_x$. The poly(acetylenicphosphazenes) are readily brominated and are potential intermediates to a variety of novel polyphosphazenes, such as poly(fluoroorganophosphazenes) and poly(ethylenicphosphazenes).

Preparation of cyclic or linear perfluoroalkoxyphosphazenes was unsuccessful. Alkali perfluoroalkoxides were prepared in situ, via alkali fluorides and perfluorocarbonyl compounds, and reacted with dihalophosphazenes, $(Cl_2PN)_3$, $(F_2PN)_3$, and $[Cl_2PN]_n$ polymer.

Chlorination of trifluoroethoxyphosphazenes as a route to cyclic or linear perfluoroethoxyphosphazenes was unsuccessful.

Preparation of perfluoroalkylphosphazenes via organometallic reagents and cyclic or linear dichlorophosphazenes was unsuccessful. The organometallic reagents were selected from R_fMgBr, R_fMgI, R_fCu, and R_fZnI, where R_f = n-C_3F_7.

A cyclic perfluoroaryloxyphosphazene $[(C_6F_5O)_2PN]_3$, was prepared but failed to polymerize at elevated temperature. Directed preparation of linear $[(C_6F_5O)_2PN]_n$ polymer by substitution of $[Cl_2PN]_n$ polymer afforded an impure intractable product.

TABLE OF CONTENTS

POLY(FLUOROORGANOPHOSPHAZENES)

1.0 BACKGROUND AND INTRODUCTION

Horizons Research Incorporated has conducted several research programs towards the development of several poly(fluoroalkoxyphosphazene) copolymers as low temperature, high strength, solvent resistant elastomers [Refs. 1-4]. This work has advanced to a point where the utility of these materials for the Army's longstanding requirement for fuel and solvent resistant "Arctic Rubbers" is about to be realized. Other programs sponsored by the Army and Naval Air Systems Command have led to development of these materials as seals and O-rings for use to 350°F. [Refs. 5-7].

Future materials requirements, particularly for aerospace applications, specify elastomers which can perform in the 500°F to 600°F temperature region and beyond. Although attention at Horizons has been focused on development of the poly(fluoroalkoxyphosphazenes) for the -65°F to 350°F temperature range, substantial data exists which could justify the belief that the polyphosphazenes are excellent potential candidates for service in the region of 500°F and beyond.

Model oligomeric compounds such as $[(C_3F_7CH_2O)_2PN]_3$ are stable to reflux at 650°F [Ref. 8]. Studies conducted with Cl_2PN oligomer/polymer mixtures [Ref. 9] at 1100°F gave no indication of products which contained bonds other than those contained in the starting mixtures. Short chain linear Cl_2PN polymers which were end capped with metal halides [Ref. 10] have long term thermal stability at 1000°F in the absence of moisture.

The stability of the phosphorus-nitrogen bond and of the bonds in the side chains in current materials indicates these materials may be suitable for consideration for a 600°F elastomer. The reason stability to 600°F has not been achieved in existing poly(fluoroalkoxyphosphazenes) may be related to one of two problems. The first problem is that poly(fluoroalkoxyphosphazene) elastomers have a tendency to undergo depolymerization at elevated temperatures to form cyclic oligomers of the same chemical composition. Polyphosphazene homopolymers $[(CF_3CH_2O)_2PN]_n$ and $[(C_6H_5O)_2PN]_n$ also molecularly degrade thermally, cyclic oligomers being the

predominant products [Ref. 11,12]. The depolymerization rate varies from sample to sample, even though the samples are prepared in a manner intended to give identical materials. Depolymerization has been shown to be retarded by judicious compounding and crosslinking, but improvements realized have only increased serviceability to 400°F, at best.

The second problem that limits poly(phosphazene) technology concerns polymer structure. The presence of $-OCH_2-$ bonds in the known poly(fluoroalkoxy phosphazenes) may contribute to oxidative and/or thermal degradation. Certainly such sites would be more susceptible to chemical and solvent attack relative to a perfluorinated alkyl or ether site. Perfluorohydrocarbon groups are desirable because of their inherent hydrolytic and chemical resistance as well as their ability to withstand temperatures of at least 700°F. [Refs. 13,14].

Under Contract No. F44620-76-C-0101 Horizons Research has investigated the feasibility of preparing polyphosphazenes which would be serviceable in the 500°F to 600°F range and possess outstanding low temperature properties and solvent and chemical resistance characteristics of the known poly(fluoroalkoxyphosphazene) elastomers.

Successful development of a 600°F elastomer would lead to greatly improved gaskets, O-rings, seals, foams, hoses, etc., all necessary for continued advanced aerospace progress. This technology would also be applicable to low molecular weight materials such as lubricants and fluids.

Development of improved poly(phosphazenes) has primarily been structural in origin, that is, preparation of totally new -P=N- materials. Syntheses of poly(perfluoroalkoxyphosphazenes), poly(perfluoroaryloxyphosphazenes) and poly(perfluoroalkylphosphazenes) have been explored. Two general approaches were considered; firstly, preparation of an intermediary cyclic oligomer which would subsequently be thermally polymerized as shown in equation (1); and secondly, direct substitution on a linear poly(dihalophosphazene) as shown in equation (2).

$$(Cl_2PN)_3 + 6R_fM \xrightarrow[-6MCl]{} [(R_f)_2PN]_3$$

$$[(R_f)_2PN]_3 \xrightarrow[(cat.)]{\Delta} [(R_f)_2PN]_n \qquad (1)$$

$$(Cl_2PN)_3 \xrightarrow[(cat.)]{200°C} [Cl_2PN]_n \qquad (2)$$

$$[Cl_2PN]_n + 2nR_fM \xrightarrow[-2nMCl]{} [(R_f)_2PN]_n$$

Where R_f is selected from CF_3O, C_2F_5O, C_6F_5O,

$CF(CF_3)_2O$, C_3F_7, and

M is selected from Na, K, Cs, ZnI, MgI, MgBr

A novel approach developed near the end of the contract year, and not shown above, involved attempted preparation of poly-(acetylenicphosphazenes). Such materials are potential precursors to poly(fluoroorganophosphazenes), although not necessarily poly(perfluoroorganophosphazenes). The preparation of candidate poly(phosphazenes) via poly(acetylenic phosphazenes). is shown in Scheme 1.

It was anticipated that once the problems associated with the preparation of homopolymers (which will probably not be elastomers) are overcome, then the preparation of copolymers will be attempted. Mixtures of different R_f groups or R_fO- groups would be used to prepare copolymers in an effort to disrupt crystallinity, in instances where elastomers were desired.

2.0 DISCUSSION AND RESULTS

Summary of Highlights Under Contract No. F44620-76-C-0101:

(1) Both cyclic and polymeric acetylenic phosphazenes can be prepared by reaction of alkali acetylide salts with dihalophosphazene precursors. The poly(acetylenicphosphazenes) are easily halogenated and are potential intermediates to poly(fluoroalkyl- and fluoroaryl phosphazenes).

(2) Preparation of cyclic or linear perfluoroalkoxyphosphazenes was unsuccessful. This is attributed either to instability of alkali perfluoroalkoxides and/or side reactions.

(3) Chlorination of trifluoroethoxyphosphazenes as a route to perfluoroethoxyphosphazenes was unsuccessful.

(4) Preparation of perfluoroalkyl organometallics and subsequent reaction with dihalophosphazenes was unsuccessful.

(5) Hexakis(pentafluorophenyl) cyclotriphosphazene, $[(C_6F_5O)_2PN]_3$, was prepared but failed to polymerize at elevated temperatures. A poly(perfluoroaryloxyphosphazene) was prepared but the product was intractable and impure.

High molecular weight poly(phosphazenes)such as poly(fluoroalkoxyphosphazenes) and poly(aryloxyphosphazenes) are generally prepared by reaction of the appropriate sodium alkoxide or aryloxide salt(s) with high molecular weight poly(dichlorophosphazene) as shown in equation (3).

$$2n\ RONa + [Cl_2PN]_n \longrightarrow [(RO)_2PN]_n + 2nNaCl \qquad (3)$$

Although high molecular weight plastics and elastomers would eventually be desired for a variety of Air Force needs, high molecular weight $[Cl_2PN]_n$ polymer was not used as a starting material for the attempted synthesis of poly(fluoroorganophosphazenes). Instead, hexachlorocyclotriphosphazene, $(Cl_2PN)_3$, and low molecular weight $[Cl_2PN]_n$ polymer were employed. The rationale for using the cyclic model compound was as follows: Starting material and product(s) could be monitored via gas chromatography, products

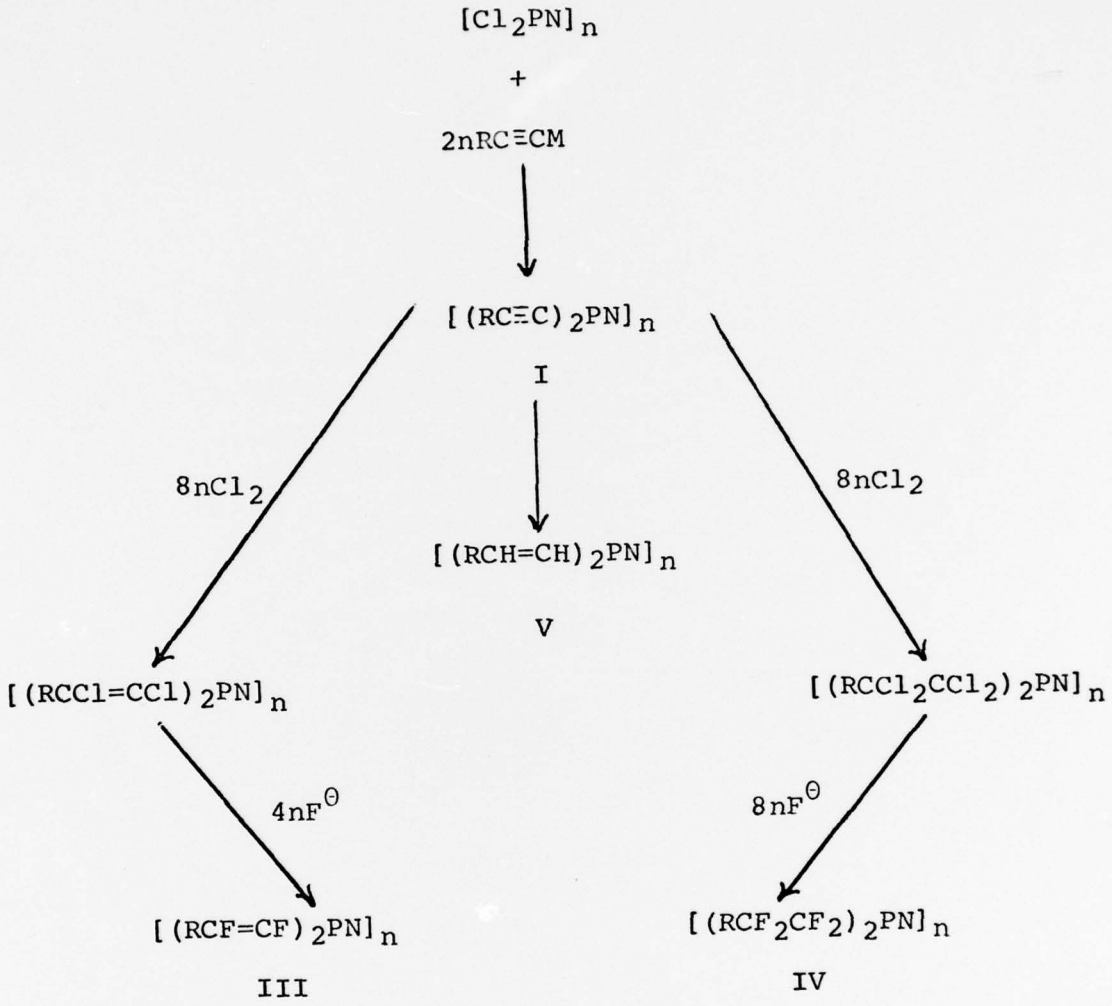
are easier to isolate and purify than polymer analogs, inability to substitute the cyclic phosphazene would almost surely be indicative of inability to substitute $[Cl_2PN]_n$ polymer, and desired hexakis-(perfluoroorgano)cyclotriphosphazenes might be capable of undergoing thermal ring-opening polymerization. Low molecular weight $[Cl_2PN]_n$ polymer was employed to avoid viscosity and diffusion related problems.

Preparation of several types of poly(perfluoroorganophosphazenes) shown below was attempted.

Phosphazene Type	Generic Formula
Perfluoroalkoxy	$(R_fO)_2PN$, where R_f = CF_3, C_2F_5, $F-\overset{CF_3}{\underset{CF_3}{\overset{\vert}{\underset{\vert}{C}}}}-$
Perfluoroalkyl	(R_f) PN, where R_f = $\underline{n}$-C_3F_7
Perfluoroaryloxy	$(Ar_fO)_2PN$, where Ar = C_6F_5

As discussed in Sections 2.2-2.4 little or no success was encountered in the preparation of cyclic or linear polymeric species of any of these types.

The lack of success in preparing poly(perfluoroorganophosphazenes) led to investigation of a novel approach to preparing polyphosphazenes not containing perfluoroorgano ligands bound to phosphorus, but which could potentially be acceptable for Air Force needs. The chemistry of this potential class of materials is outlined in Scheme 1 of Section 1.0. The key factor in this scheme is the preparation of poly(acetylenicphosphazenes). Work on these materials came very late in the program. The results are very encouraging and future work appears justified. Therefore, this phase of work will be discussed initially in this section.



Where R is selected from lower alkyl, phenyl, $-CO_2C_2H_5$, CF_3, and
M is selected from Li, Na

SCHEME 1

Preparation of Poly(acetylenicphosphazenes) and Derivatives

2.1 Poly(Acetylenicphosphazenes), $[RC\equiv C)_2PN]_n$

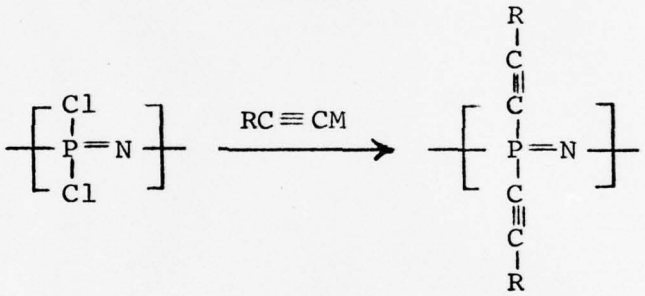
Highlights in this area are summarized:

(1) Both $(Cl_2PN)_3$ trimer and $[Cl_2PN]_n$ polymer undergo rapid reaction with alkali phenylacetylide salts to give acetylenic phosphazene products.

(2) The acetylenic phosphazene materials react with bromine, have high melting points, and show good thermal stability.

(3) Attempted substitution of P-Cl by $HC\equiv C-CO_2C_2H_5$ fails because of the high reactivity of the ester in the presence of even weakly basic materials.

Poly(acetylenicphosphazenes) (I) should be preparable by reaction of alkali acetylide salts with $[Cl_2PN]_n$ polymer as shown in Equation (4):



(4)

I

where R is alkyl, aryl, and derivatives thereof.

The novel polymers (I) should be versatile intermediates for a variety of novel polymers as shown in Scheme 1 of Section 1.0. Use of different R's would give copolymers or higher interpolymers. This is important for decreasing crystallinity and achieving the elastomeric state.

Poly(fluoroalkylphosphazenes) such as $[(RCF=CF)_2PN]_n$ (III) and $[(RCF_2CF_2)_2PN]_n$ (IV) should have good thermal and solvent resistance and thus be capable of meeting many stringent Air Force materials requirements. On the other hand, the unsaturated polymers $[(RCH=CH)_2PN]_n$ (V) and $[(RC=C)_2PN]_n$ could show interesting electrical properties because of the extended conjugated system. Electrical effects in polymers V should be subject to

substituent changes in the meta or para positions when R = C_6H_5. Polymers V, possibly even polymers I, might be candidates in gas detection systems. McDonnell Douglas Aircraft has reported that some poly(phenylacetylenic) materials may be useful in gas detector systems [Ref. 15].

The successful preparation of soluble phosphorus-carbon containing polyphosphazenes from $[ClPN]_n$ polymer has not been described previously. Reaction with organometallic reagents has led to extensive molecular degradation [Refs 16, 17]. Soluble phosphorus-carbon containing polyphosphazenes have been synthesized by other routes [Refs. 18-21]. In most of these instances phenylated polyphosphazenes were prepared from $[F_2PN]_n$ polymer [Ref. 18], by polymerization of the costly intermediate $(C_6H_5)F_5P_3N_3$ [Ref. 19], or from $C_6H_5PCl_2$ by reaction with sodium azide [Ref. 20]. The $[F_2PN]_n$ polymer is produced in low yield by the very high temperature (ca. 350°C) polymerization of $[F_2PN]_3$ which is not commercially available, unlike $(Cl_2PN)_3$. Lastly, arylated polyphosphazenes with degrees of polymerization of seven or less have been described [Ref. 21]. These polymers were prepared by several condensation procedures, namely reaction of bisphosphine and a diazide, reaction of a bis(dichlorophosphorane) and a diamine, reaction of a bisphosphine with a diamine in the presence of carbon tetrachloride.

The initial work conducted on poly(acetylenicphosphazenes) utilized sodium phenylacetylide and $(Cl_2PN)_3$ in tetrahydrofuran solvent. A highly substituted product was obtained which contained halogen. Similar substitution of $(Cl_2PN)_3$ could be achieved using the more soluble lithium phenylacetylide. This salt could be prepared by reaction of the sodium salt with lithium chloride or preferably by reaction of phenylacetylene with lithium metal.

A product was obtained which contained 61.8% carbon and 6.0% chlorine and which showed a strong IR absorption at 2170 cm^{-1}, attributed to the -C≡C- group. This product took up about 57% bromine upon reaction with bromine in carbon tetrachloride at room temperature. The brominated product no longer showed an IR absorption at 2170 cm^{-1}.

The reaction of lithium phenylacetylide was extended to low molecular weight ([n] = 0.08 dl/g) $[Cl_2PN]_n$ polymer at ambient temperature and at reflux (ca. 68°C). Soluble and insoluble (presumably crosslinked polymer) fractions resulted which were spectrally (IR) identical and which did not melt up to 320°C. The soluble fraction from the room temperature run had an intrinsic viscosity [n] of 0.06 dl/g, indicative of low molecular weight polymer. Percent chlorine content

of the soluble and insoluble fractions were 2.9% and 6.1%, respectively, (%Cl in Cl_2PN is 61). Surprisingly, the overall product yield exceeded theory. This may be due to further addition of $C_6H_5C\equiv CLi$ to $P\text{-}C\equiv C\text{-}C_6H_5$ sites. Good isothermal aging of the completely unoptimized fractions was obtained. Weight loss in air after 24 hours @ 200°C was 6% and 0% for the soluble and insoluble fractions, respectively.

Attempts to react the model trimeric $(Cl_2PN)_3$ with ethyl propiolate ($HC\equiv CCO_2C_2H_5$) were unsuccessful due to the great propensity of the propiolate to undergo base catalyzed addition reactions. The weakly basic pyridine was sufficient to cause rapid side reaction of ethyl propiolate in the absence of $(Cl_2PN)_3$.

2.2 Attempted Preparation of Poly(perfluoroalkoxyphosphazenes), $[(R_fO)_2PN]_n$

Highlights in this area are summarized:

(1) The reactions between alkali perfluoroalkoxides with either $[Cl_2PN]_n$ polymer, $(Cl_2PN)_3$ trimer, or $(F_2PN)_3$ trimer did not yield the desired perfluoroorganophosphazenes.

(2) Major problems appear to be associated with limited stability of the alkali perfluoroalkoxides and to side reactions affording inorganic product(s).

(3) Chlorination of $(CF_3CH_2O)_2(PN)_3$ or of $[(CF_3CH_2O)_2PN]_n$ polymer above 100°C using peroxide catalyst is not a viable route for the preparation of CF_3CCl_2O-containing phosphazenes.

Ideally poly(perfluoroalkoxyphosphazenes) could be prepared by reaction of halophosphazene with an alkali perfluoroalkoxide as shown in Equations (5) and (6).

$$(Cl_2PN)_3 + 6R_fOM \longrightarrow [(R_fO)_2PN]_3 \quad \text{(cyclic)} \qquad (5)$$

$$[Cl_2PN]_n + 2n\ R_fOM \longrightarrow [(R_fO)_2PN]_n \xleftarrow{\Delta\ \text{(cat.)}} \qquad (6)$$

where M = Na, K, Cs
R_f = perfluoroalkyl

The perfluoroalkoxide salts would be considerably less basic and therefore less reactive than previously used polyfluoroalkoxide salts derived from CF_3CH_2OH or $H(CF_2CF_2)_nCH_2OH$ alcohols, where n = 1, 3 or 5. An additional problem is that when R_f is straight chain, the R_fOM salts become thermally unstable [Refs. 22, 23]. Increasing temperature increases the vapor pressure of the system because of a shift of the equilibrium to the left. The preparation of R_fOM salts is shown in Equation (7).

$$R'_fC(=O)F + MF \rightleftharpoons R'_fCF_2OM \qquad (7)$$

where M = K, Cs
R'_f = F, CF_3 and
$R'_fCF_2 = R_f$

Preparation of alkali heptafluoroisopropoxide salts from commercially available hexafluoroacetone and alkali fluorides is well known as shown in Equation (8). These isopropoxide salts are stabler than R_fCF_2OM salts and have been used in substitution reactions of organic halides at temperatures of about 80°F [Ref. 24].

$$(CF_3)_2C=O + MF \longrightarrow (CF_3)_2FC\text{-}O\text{-}M \qquad (8)$$

M = K, Cs

However, the extremely weak basicity and increased steric hindrance of this salt would be expected to significantly reduce reaction rates with P-Cl sites compared to the primary R_fOM salts, all other things being equal.

Preparations of CF_3OM and C_2F_5OM and subsequent reactions with halophosphazenes were carried out in a small autoclave. Excess carbonyl fluoride or trifluoroacetyl fluoride was introduced at dry ice temperatures to a mixture of solvent [bis(2-methoxyethyl) ether (diglyme) or acetonitrile] and alkali fluoride. The autoclave was mildly agitated overnight prior to addition of chlorophosphazene and additional

organo fluoride reagent. The frequent caking of solids at the bottom of the autoclave indicated very inadequate mixing. It is strongly recommended that any future work in this area be carried out with a stirred autoclave.

Cesium pentafluoroethoxide was prepared from CsF and CF_3COF and reacted with $(F_2PN)_3$ in CH_3CN at 25-80°C, and also with low molecular weight $[Cl_2PN]_n$ polymer. An identical product, which did not show a P=N band in the infrared and is believed to be totally inorganic, was isolated from both reactions. The $[Cl_2PN]_n$ polymer had an intrinsic viscosity of 0.17 dl/g in benzene at 30°C.

Cesium trifluoromethoxide was reacted with $[Cl_2PN]_n$ polymer in CH_3CN at 25-77°C. A solid product was obtained which again appeared to be totally inorganic as indicated by elemental and IR analysis.

The above reactions were likewise disappointing when diglyme was substituted for acetonitrile as solvent. Cesium trifluoromethoxide and pentafluoroethoxide were reacted with $[Cl_2PN]_n$ polymer in diglyme at 25-80°C. Either little or no reaction was obtained with or without Crown ether catalyst. An inorganic solid was obtained which was similar to a solid isolated from a prior reaction between cesium pentafluoroethoxide and $(F_2PN)_3$ trimer. This latter solid was shown to be inorganic by elemental and IR analyses.

The reaction of potassium pentafluoroethoxide with $(Cl_2PN)_3$ at 25-76°C in diglyme and with Crown ether catalyst afforded a small amount of solid which in part could be the desired perfluoroethoxy polymer as suggested by IR. However, these results are not conclusive. The product appeared to hydrolyze on workup with water. It may be necessary to carry out the workup below room temperature.

Chloride ion might be detrimental to the stability of a poly(perfluoroorganophosphazene) formed via reaction of $[Cl_2PN]_n$ polymer with a perfluoroalkoxide. To safeguard against this possibility, an attempt was made to prepare the $[F_2PN]_n$ polymer from the $[Cl_2PN]_n$ polymer by reaction with KF in diglyme at 25-88°C using a Crown ether catalyst. However, the $[F_2PN]_n$ polymer precipitated at the end of the reaction. This precipitation was due to insolubility of the polymer in diglyme since it could be dissolved in Freon E-3. However, it would be difficult to dissolve the perfluoroalkoxides in E-3 for subsequent reaction with the $[F_2PN]_n$ polymer.

The reaction between potassium perfluoroisopropoxide (formed in situ by reaction of KF and hexafluoroacetone) and $(Cl_2PN)_3$ trimer in diglyme at 25-79°C using a Crown ether as catalyst did not yield the desired perfluoroalkoxy trimer. Gas chromatography on the reaction mixture before workup exhibited only the diglyme peak, no other products were detected. It is possible that the desired product is unstable at room temperature or above and the reaction work-up may have to be conducted below room temperature.

To test this hypothesis the reaction was repeated at a lower temperature (0-5°C) in tetrahydrofuran. Again, gas chromatographic analysis indicated substantial conversion of trimer but no formation of volatile products. A product was obtained in low yield which was insoluble in tetrahydrofuran or Freon E-3, but was soluble in water. These properties coupled with lack of gas chromatographic response rule out desired product. Further characterization was not undertaken.

Possible product instability of $-OC(CF_2)_2F$ containing heterocycles in the presence of reactants and/or inorganic materials has been indicated in the literature [Ref. 25]. Specifically, 2,4,6-tris(perfluoroisopropoxy)-s-triazine was prepared from KF, CF_3COCF_3 and diglyme by addition of cyanuric chloride, $(ClCN)_3$, maintaining the temperature at -10°C to 3°C, followed by an ice temperature workup. In this manner the high boiling (187°C) product could be obtained in high yield. Higher reaction or workup temperatures led to decreased yields.

The reaction of potassium perfluoroisopropoxide with $(F_2PN)_3$ at 25-65°C was likewise discouraging. Gas chromatographic analyses indicated consumption of $(F_2PN)_3$ but did not indicate formation of volatile products. The $(F_2PN)_3$, which had been prepared by reaction of $(Cl_2PN)_3$ with NaF, was selected for the above reaction because of the lower steric requirement of F over Cl and to rule out possible side reactions due to nucleophilic attack by chloride ion on product.

The inability to prepare perfluoroalkoxy phosphazene via a reaction with perfluoroalkoxides led to exploration of an alternate synthesis. In this approach, as shown in Equations (9) and (10), the cyclic oligomer $[(CF_3CF_2O)_2PN]_3$

was desired as a model for thermal ring opening polymerization.

$$(Cl_2PN)_3 + 6CF_3CH_2ONa \longrightarrow [(CF_3CH_2O)_2PN]_n \quad (9)$$

$$\xrightarrow[\text{cat.}]{Cl_2} [(CF_3CCl_2O)_2PN]_3 \xrightarrow{FO} [(CF_3CF_2O)_2PN]_3 \quad (10)$$

The chlorination of analogous materials has been reported [Ref. 8]. Subsequent perfluorination should then be possible by reaction with KF in a high boiling polar aprotic solvent. This halogen interchange is well known [Refs. 26, 27].

Chlorination at 90°C was attempted with Cl_2 in carbon tetrachloride-hexachloroethane using benzoyl peroxide catalyst. A variety of high boiling specie, presumably polychlorinated derivatives, were produced as evidenced by gas chromatographic analysis at 250°C. Repetition of this work using chlorine which had been predried by passage through concentrated sulfuric acid led to relatively little reaction. Complete substitution of available -CH sites to afford the single desired product did not appear to warrant further investigation.

The attempted chlorination of $[(CF_3CH_2O)_2PN]_n$ polymer in Freon E-3 at 120-152°C was likewise discouraging. A product was obtained which contained only 1.9% chlorine.

2.3 Attempted Preparation of Poly(perfluoroalkylphosphazenes), $[(R_f)_2PN]_n$

Highlights in this area are summarized:

(1) The reactions between C_3F_7MgBr and $[Cl_2PN]_3$ gave recovered trimer and an undesired product. The in situ preparation of C_3F_7MgI from C_3F_7I and Mg in the presence of trimer cannot be carried out because trimer reacts with magnesium.

(2) A suitable formation of C_3F_7Cu for reaction with the $[Cl_2PN]_3$ trimer or $[Cl_2PN]_n$ polymer did not succeed.

(3) Reaction of C_3F_7ZnI with $[Cl_2PN]_n$ polymer may give some of the desired interchange.

Another approach to form perfluorinated polyphosphazenes involved in situ preparation of organometallics, such as R_fMgBr, R_fMgI, R_fCu, and R_fZnI, for their subsequent reactions with $(Cl_2PN)_3$ trimer or $[Cl_2PN]_n$ polymer.

The desired perfluoroalkyl Grignard could be generated via exchange reactions between C_6H_5MgBr or C_2H_5MgBr and $\underline{n}$-C_3F_7I. These reactions are known to be quantitative and rapid in ether solvents [Refs. 28,29]. The interchange as shown in equation (11) must be carried out at very low temperatures because of the instability of the R_fMgBr reagent.

$$RMgBr + \underline{n}\text{-}C_3F_7I \xrightarrow[-70°C \text{ to } -40°C]{} \underline{n}\text{-}C_3F_7MgBr + RI \qquad (11)$$

Poly(perfluoroalkylphosphazenes) would be expected to show high thermal stability and excellent resistance to strong acids. Poly[bis(trifluoromethyl)phosphazene], $[(CF_3)_2PN]_n$, of unknown molecular weight has been prepared from bis(trifluoromethyl)azidophosphine, $(CF_3)_2PN_3$ [Ref. 30], and from bis(trifluoromethyl)dichlorophosphinic amide, $(CF_3)_2P(Cl_2)NH_2$ [Ref. 31]. The polymer decomposes near 380°C and is stable to boiling sulfuric acid. The two direct routes for the preparation of $[(CF_3)_2PN]_n$ polymer were not considered for the current study because starting materials are difficult to prepare, scale-up could present a problem, and little is known about molecular weight control.

The reaction involving the C_6H_5MgBr, $\underline{n}$-C_3F_7I and trimer in ether at 5-8°C gave recovered trimer and a solid which by IR was not the desired product. Another reaction involving C_2H_5MgBr under similar conditions gave primarily recovered trimer and a small amount of an unknown which showed no P-N absorption in the IR. From the above results, it appears the $\underline{n}$-C_3F_7MgBr decomposes at a faster rate than its desired reaction with trimer.

Any attempt to form $\underline{n}$-C_3F_7MgI in situ from $\underline{n}$-C_3F_7I and Mg for its subsequent reaction with $(Cl_2PN)_3$ trimer would not succeed in the presence of trimer. This is because a rapid reaction occurs between trimer and Mg in tetrahydrofuran at room temperature.

The formation of $\underline{n}$-C_3F_7Cu from $\underline{n}$-C_3F_7I and Cu using complexing agent (diglyme and γ-collidine) at 25-125°C did not succeed. Conventional complexing agents such as N,N-dimethylformamide or dimethylsulfoxide were not employed because they can interact with trimer [Ref. 32]. Diglyme and γ-collidine did not appear to complex the $\underline{n}$-C_3F_7Cu sufficiently to prevent its decomposition at elevated temperatures.

Lastly, the zinc organometallic reagent n-C_3F_7ZnI was prepared from Zn and n-C_3F_7I for study with chlorophosphazenes. This zinc reagent was expected to have good organic solubility as well as increased thermal stability relative to the corresponding Grignard reagent. Reaction of n-C_3F_7ZnI with low molecular weight $[Cl_2PN]_n$ polymer (η=0.10 dl/g) at 35°-120°C led to isolation of a chloroform soluble viscous brown oil. Infrared indicated P=N and $-\overset{O}{\overset{\uparrow}{P}}-NH$ bands, and possibly P-Cl bands. Interference made it difficult to determine the presence of CF_3 or CF_2 absorption. The presence of incomplete substitution was confirmed by a positive Beilstein test and by crosslinking of the product upon standing at room temperature for two days. In an attempt to attain a higher degree of substitution the reaction was repeated at 100-120°C for 5 days. Essentially no chloroform soluble phosphazene product was isolated.

2.4 Poly(perfluoroaryloxyphosphazenes), $[(C_6F_5O)_2PN]_n$

Highlights in this area are summarized:

(1) In the preparation of the $[(C_6F_5O)_2PN]_n$ polymer from $[Cl_2PN]_n$, only impure polymer in low yield was obained.

(2) The thermal polymerization of $[(C_6F_5O)_2PN]_3$ trimer did not succeed.

In order to circumvent the uncertainties of reagent purity and instability encountered with the perfluoroalkoxides described in Section 2.2 sodium pentafluorophenoxide was chosen for study for reaction with chlorophosphazenes.

The reaction of sodium pentafluorophenoxide with low molecular weight $[Cl_2PN]_n$ polymer in diglyme at 25-135°C gave a 13% yield of product, thought to be the impure $[(C_6F_5O)_2PN]_n$ polymer, as evidenced by IR and elemental analyses. The relatively low chlorine content (0.29%) was indicative of effective substitution. However, the discrepancies of carbon and fluorine content with theory indicate substantial side reaction had occurred.

The sealed tube (318-340°C) polymerization of $[(C_6F_5O)_2PN]_3$ trimer (0.4 g), prepared from $(Cl_2PN)_3$ and C_6F_5ONa, afforded a brown solid which was not the desired product by IR analysis. A rapid decomposition occurred as evidenced by the disintegration of two sealed tubes when larger quantities (1 g) of trimer were heated in smaller volumes.

3.0 CONCLUSIONS AND RECOMMENDATIONS

Preparation of novel perfluoroorganophosphazenes via substitution reactions of dihalophosphazenes does not appear to warrant further investigation.

Novel poly(acetylenicphosphazenes) are preparable via reactions of alkali acetylide salts and dihalophosphazenes. Poly-(acetylenicphosphazenes) are potential candidates for the preparation of poly(fluoroorganophosphazenes) and poly(ethylenic-phosphazenes). Therefore, this area requires further study to determine the full range of this potential. Recommended work to be done is as follows:

(1) Study reaction parameters (mode of addition, solvent, temperature) to eliminate cross-linking and to achieve complete substitution of P-Cl sites.

(2) Determine effects of acetylinic structure on substitution reaction and on polymer properties.

(3) Convert poly(acetylenicphosphazenes) to ethylenic and polyfluorinated derivatives.

(4) Determine likely applications for selected candidate polymers.

4.0 EXPERIMENTAL *

4.1 Attempted Preparation of Poly[bis(phenylethynyl)-phosphazene] $[(C_6H_5C\equiv C)_2PN]_n$

Lithium phenylacetylide was prepared under nitrogen by reaction of lithium metal (1.73 g, 0.25 mol) with phenylacetylene (28.1 g, 0.275 mol) in dry tetrahydrofuran (100 ml). The reaction was completed by refluxing one hour. The lithium phenylacetylide solution (125 ml) was added dropwise under nitrogen to a solution of $[Cl_2PN]_n$ polymer (7.94 g, 0.0685 mole equiv.; [n] = 0.08 dl/g benzene, 30°C) in benzene (50 ml) containing phenylacetylene (5 ml). The temperature was maintained at 23-31°C. Approximately one-half (100 ml) of the reaction mixture was poured off for workup while the remainder was refluxed (68.5°C) for 32 hours. The poured off portion was suction filtered to give black solids which weighed 9.8 g after washing with methanol (3 x 100 ml) and vacuum drying. The black filtrate was evaporated to give a black gummy solid (15.3 g) to which petroleum ether (150 ml) was added. The petroleum ether insoluble solid was filtered off, washed with methanol (6 x 40 ml), and vacuum dried to afford 6.8 g [Sample 2495-35A]. The petroleum ether filtrate solids dried to 3.0 g [Sample 2495-35B] which was soluble in tetrahydrofuran. Infrared spectra of the A and B samples were identical. Both samples gave positive Beilstein, with A giving a much stronger test.

The refluxed portion of the reaction could not filter readily and was diluted with tetrahydrofuran to a volume of 200 ml and then centrifuged. The workup then essentially followed as described above to give Samples 2495-36A (10.2 g) as a dark brown solid and 2495-36B (2.6 g) as a lighter brown solid soluble in tetrahydrofuran (THF). The results are tabulated.

*The examples in this section have been selected as representative of the chemistry discussed in Sections 2.1 - 2.4.

Sample No. 2495-	Reaction Temperature	Yield (g)	THF Solubility	Elemental Analysis[a] % C	% H	% Cl
-35A	Ambient	6.8	-	66.28	4.02	6.12
-35B		3.0	+[b]	58.21	4.58	2.85
-36A	Reflux	10.2	-	--	--	--
-36B		2.6	+	--	--	--

(a) Calculated for $[(C_6H_5C\equiv C)_2PN]_n$: C, 77.73; H, 4.05; Cl, 0.

(b) [n] = 0.06 dl/g, 30°C.

The THF insoluble fractions were also insoluble in hexamethylphosphoramide (swells) and acetic acid, but slowly dissolved in conc. H_2SO_4.

4.2 Attempted Preparation of Hexakis(heptafluoroisopropoxy)-cyclotriphosphazene

Procedure A, via $(Cl_2PN)_3$:

The potassium heptafluoroisopropoxide was prepared as follows: Using a dry ice condenser hexafluoroacetone (28.7 g, 0.172 mole) was bubbled into a mixture of potassium fluoride (7.25 g, 0.125 mole; dried at 200°C) and dry tetrahydrofuran (100 ml) at 19-30°C. To the resulting stirred solution was added over 1 hour a solution of hexachlorocyclotriphosphazene (7.25 g, 0.125 equiv. P-Cl) in tetrahydrofuran (30 ml). The reaction was maintained at 0-5°C for 3 hours and then placed in the freezer (-18°C) for 2-1/2 days. Gas chromatographic analysis showed approximately 50% trimer conversion and no products after 3 hours at ice temperature. The reaction

mixture was filtered at ice temperature and the filtrate concentrated by rotary evaporation to afford an opaque liquid (4.8 g) which was insoluble in tetrahydrofuran or Freon E-3 but was soluble in water and which did not show any significant volatile components via gas chromatography. Desired product should have different solubilities and be detectable via gas chromatography; therefore, further characterization was not undertaken.

Procedure B, via $(F_2PN)_3$

The potassium heptafluoroisopropoxide was prepared as described above using potassium fluoride (6.44 g, 0.111 mole) dry diglyme (50 ml) and hexafluoroacetone (20.0 g, 0.121 mole). Then hexafluorocyclotriphosphazene (9.22 g, 0.037 mole) was added and the reaction stirred 2 days at room temperature and heated 18 hours at 65°C. The reaction mixture was cooled, white solid filtered off, and the filtrate poured into ice water and extracted with ethyl ether. The ether layer was dried with Na_2SO_4 and ether distilled off to afford a trace yield of product. Gas chromatographic analysis of the reaction prior to workup showed substantial conversion of $(F_2PN)_3$ with only trace quantities of other volatile components.

4.3 Attempted Preparation of Poly[bis(n-heptafluoropropyl)-phosphazene]

A solution of n-heptafluoropropyl zinc iodide was prepared as follows: Under nitrogen with good stirring a solution of n-heptafluoropropyl iodide (Fairfield Chemical Co.; 25 g, 0.0845 mole) in diglyme (17 ml) was added over 2 hours at 20°C to a mixture of zinc dust (11.1 g, 0.170 mole; activated by washing twice for 1 minute with 2% aqueous HCl followed by water and methanol washing and vacuum drying). After stirring overnight, the mixture was filtered in a dry box. Titrimetric analysis of the clear light amber-yellow liquor indicated 1.53 meq. organometallic reagent per milliliter solution. A 40% solution (7.8 g) of poly(dichlorophosphazene) (3.1 g, 0.027 mole equiv.; [n] = 0.10 dl/g, benzene, 30°C) in diglyme (6 ml) was added dropwise at 35-60°C to the organometallic reagent (43 ml, 0.066 mole). The reaction was heated 20 hours at 120°C. Thereafter, it was cooled to room temperature, suction filtered, and solids washed with diglyme and petroleum ether. The insoluble white

crystalline residue weighed 0.68 g. The filtrate was initially concentrated using a rotary evaporator followed by vacuum pump at 45°C. The resultant residue was a brown viscous oil. The residue was diluted with chloroform (50 ml) and washed thrice with ice cold 20% aqueous HCl (50 ml). The chloroform layer was dried over Na_2SO_4 and solvent evaporated to give a residue of 3.6 g. Infrared indicated -P=N- bands, some -P(=O)-NH bands and a questionable P-Cl band. Interference prevented detection of CF_3 or CF_2 absorptions. The product showed a positive Beilstein test. The sample crosslinked upon standing over the weekend at room temperature.

The above experiment was repeated with the following modifications: The organo zinc reagent was added gradually to the heated (80-100°C) solution of $[Cl_2PN]_n$ polymer and the reaction maintained at 118 hours at 100-120°C. After workup, the chloroform soluble product weighed 0.8 g. and was largely diglyme based on infrared analysis.

4.4 Reaction of $(Cl_2PN)_3$ with Sodium Pentafluorophenoxide

The sodium salt of pentafluorophenol was prepared under nitrogen by adding a solution of pentafluorophenol (20.3 g, 0.110 mole) in diglyme(15 ml) to a mixture of sodium hydried (2.4 g, 0.10 mole) and diglyme (55 ml) at 5-10°C. After 1 hour at 20°C a solution of $(Cl_2PN)_3$ (10.5 g, 0.030 mol) in diglyme (75 ml) was added dropwise at 15-20°C. The reaction was kept at 21°C for 22 hours and heated at 70-80°C for 5 hours. The cooled reaction mixture was filtered, the solids washed with chloroform, the chloroform layer washed with ice water and dried over Na_2SO_4. Removal of solvents and addition of petroleum ether to the residue gave crystals which after filtration and drying afforded 9.1 g, m.p. 107-109°C. Cooling of filtrate afforded an additional 0.9 g., m.p. 104-106°C. The combined solid product was recrystallized from heptane to give 6.2 g, m.p. 111.5-112.5°C. Infrared and elemental analysis indicated the product to be hexakis (pentafluorophenoxy)-cyclotriphosphazene. Calculated for $[(C_6F_5O)_2(PN)]_3$; %C, 35.06; %H, 0.0; %Cl, 0.0. Found: %C, 34.68; %H, 0.10; %Cl, 0.03. The oily viscous material (23.5 g) obtained by removal of 0.9 g solid fraction could not be vacuum distilled. Chlorine analysis was 3.54%, calculated for $(C_6F_5O)_5Cl(PN)_3$, Cl 3.27%.

Polymerization of the crystalline hexakis derivatives was attempted in a capillary melting point tube at 300 to 310°C for 3-3/4 hours. Upon cooling, the melting point was 110-111°C indicative of little or no change.

4.5 Attempted Preparation of $[(C_6F_5O)_2PN]_n$

This experiment was similar to that described for the reaction of C_6F_5ONa with $(Cl_2PN)_3$, except that 25 ml diglyme was used with the pentafluorophenol and Crown ether (1 g; dibenzo-18-Crown-6) catalyst was employed. A 46% solution (10 g) of $[Cl_2PN]_n$ polymer (4.6 g, 0.08 equiv. P-Cl) in benzene diluted with diglyme (10 ml) was added at ca. 25°C to the pentafluorophenoxide solution. The reaction was maintained 19 hours at room temperature, 3 hours at 57-58°C, 17 hours at 95-100°C, and 22 hours at 127-135°C. The reaction was cooled, solids filtered and washed with ether, water and methanol to give after drying 4.3 (13% yield), m.p. >370°C. The diglyme-ether filtrate was evaporated to give an oily tar (7.6 g). The solid was insoluble in N-methylpyrrolidinone, sulfolane, hexamethylphosphoramide, and Freon E-3 (polyfluorinated ether). Infrared spectrum of the solid showed P=N and polyfluoroaryl absorptions indicative of the polymer $[(C_6F_5O)_2PN]_n$. Elemental analysis calculated for $[(C_6F_5O)_2PN]_n$: %C, 35.06; %H, 0; %N, 3.41; %F, 46.21; %Cl, 0. Found: %C, 29.91; %H, 0.31; %N, 4.88; %F, 37.07; %Cl, 0.29.

5.0 REFERENCES

1. K. Reynard, S. Rose, Final Report to AMMRC under Contract DAAG 46-70-C-0075, AMMRC CR 70-26, December 1970.

2. K. Reynard, R. Sicka, S. Rose, Final Report to AMMRC under Contract DAAG 46-71-C-0103 P00006, AMMRC CTR 73-18, May 1973.

3. S. Rose, K. Reynard, "Polyphosphazene Fluoroelastomers", ACS Meeting, Polymer Preprints, Vol. 13, August 1972.

4. S. Rose, J. Polymer Sci., Part B, 6, 837 (1968).

5. K. Reynard, R. Sicka, J. Vicic, S. Rose, Final Report to AMMRC under Contract DAAG 46-72-C-0073, September 1973, AD 773 652.

6. K. Reynard, R. Sicka, J. Vicic, S. Rose, Final Report to Naval Air Systems Command under Contract N00019-72-C-0419, June 1973, AD 762 800.

7. K. Reynard, J. Vicic, R. Sicka, S. Rose, Final Report to NAVAIR, Contract N00019-73-C-0406, March 1974, AD 781 715.

8. R. Rätz, H. Schroeder, H. Ulrich, E. Kober, C. Grundmann, J. Amer. Chem. Soc., 84, 551 (1962).

9. O. Schmitz-Dumont, Angew. Chem., 52, 498 (1939); Z. Electrochem, 45, 651 (1939).

10. G. Nichols, Rep. Conf. High Temp. Poly. Fluid Res., 1962 ASD-TDR 62-372 (1962).

11. H. Allcock, W. Cook, Macromolecules, 7, 284 (1974).

12. H. Allcock, G. Moore, W. Cook, Macromolecules, 7, 571 (1974).

13. I. Johns, E. McElhill, J. Smith, J. Chem. Eng. Data, 7, 227 (1962).

14. H. Doorenbos, H. Frick, "Thermally Stable Fluoropolymers", Final Report under Contract N00019-71-C-0331, March 1972.

References (Continued)

15. N. R. Byrd, Technical Report No. NASA CR-86047 to NASA under Contract NAS 12-15, July 1968.

16. C. F. Liu, R. L. Evans, U. S. Patent 3,169,933.

17. J. R. MacCullum, J. Tanner, J. Polymer Sci., Part A-1, 6, 3163 (1968).

18. H. R. Allcock, Unpublished Results, Pennsylvania State University.

19. H. R. Allcock, G. Moore, Macromolecules, 8, 377 (1975).

20. D. L. Herring, Chem. Ind. (London) p. 717 (1960).

21. K. L. Paciorek, D. W. Karle, R. H. Kratzer, Final Report No. NASA CR-135090 to NASA under Contract NAS3-17829, August 1976.

22. M. E. Redwood, C. J. Willis, Canad. J. Chem., 43, 1893 (1965).

23. F. Seel, R. Budenz, W. Gombler, Angew. Chem. Internat. Edit., 6, 256 (1967).

24. A. G. Pittman, W. L. Wasley, U. S. Patent 3,674,820.

25. R. W. Anderson, U. S. Patent 3,525,745.

26. G. C. Finger, C. W. Kruse, J. Am. Chem. Soc., 78, 6034 (1956).

27. J. T. Maynard, J. Org. Chem., 28, 112 (1963).

28. E. T. McBee, C. W. Roberts, A. F. Meiners, J. Amer. Chem. Soc., 79, 335 (1957).

29. D. D. Denson, C. F. Smith, C. Tamborski, J. Fluorine Chem., 3 (3-4), 247 (1973).

30. G. Tesi, C. P. Haber, C. M. Douglas, Proc. Chem. Soc., London, p. 219 (1960); U. S. Patent 3,087,937 (1963).

31. G. Tesi, C. M. Douglas, J. Amer. Chem. Soc., 84, 549 (1962).

32. B. I. Stepanov, G. I. Migachen, Zh. Obsch. Khim., 38 (1), 194 (1968); Chem. Abstr., 69, 35624h (1968).

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: AFOSR-TR- 77-0851	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): POLY(FLUOROORGANOPHOSPHAZENES).	5. TYPE OF REPORT & PERIOD COVERED: Final rept. 1 May 76 - 30 Apr 77.
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Arthur H. Gerber	8. CONTRACT OR GRANT NUMBER(s): F44620-76-C-0101
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Horizons Research Inc. 23800 Mercantile Road Cleveland, Ohio 44122	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 2303/B2, 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS: AFOSR/NC Bolling AFB, DC 20332	12. REPORT DATE: July 1977
	13. NUMBER OF PAGES: 26
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): 29p.	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

SEE REVERSE

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE 170550. UNCLASSIFIED

20.

ABSTRACT

Novel cyclic and polymeric acetylenicphosphazenes of approximate structure $[(C_6H_5C\equiv C)_2PN]_x$ have been prepared by the reaction of alkali phenylacetylide salts and dichlorophosphazenes, $[Cl_2PN]_x$. The poly(acetylenicphosphazenes) are readily brominated and are potential intermediates to a variety of novel polyphosphazenes, such as poly(fluoroorganophosphazenes) and poly(ethylenicphosphazenes).

Preparation of cyclic or linear perfluoroalkoxyphosphazenes was unsuccessful. Alkali perfluoroalkoxides were prepared in situ, via alkali fluorides and perfluorocarbonyl compounds, and reacted with dihalophosphazenes, $(Cl_2PN)_3$, $(F_2PN)_3$, and $[Cl_2PN]_n$ polymer.

Chlorination of trifluoroethoxyphosphazenes as a route to cyclic or linear perfluoroethoxyphosphazenes was unsuccessful.

Preparation of perfluoroalkylphosphazenes via organometallic reagents and cyclic or linear dichlorophosphazenes was unsuccessful. The organometallic reagents were selected from R_fMgBr, R_fMgI, R_fCu, and R_fZnI, where R_f = n-C_3F_7.

A cyclic perfluoroaryloxyphosphazene $[(C_6F_5O)_2PN]_3$, was prepared but failed to polymerize at elevated temperature. Directed preparation of linear $[(C_6F_5O)_2PN]_n$ polymer by substitution of $[Cl_2PN]_n$ polymer afforded an impure intractable product.